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The Effects of Steam Dispersion on Water Retention in the Coating System

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by

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ABSTRACT

The purpose of this study was to observe the relationship that steam dispersion has upon water holding characteristics of a starch/clay system. It is proposed that the amount of dispersion during and after depolymerization of starch will have a direct relationship with water retention. The water retention values were measured on a modified Warren tester. It was found that excess steam dispersion of the starch increased the water retention values of the coatings. However, water retention values were found to be very sensitive to %solids of the starch/clay slurry, that is, as %solids decreased, water retention of the coatings decreased. Furthermore, water retention of the coating color did not corelate with viscosity but rather to the dispersion or degree of dispersion of the starch. Also, with good starch dispersion in the slurry, groups of starch molecules, mainly hydroxyl ions can interact with water producing high water retention values. This is in the case of low %starch on water. In high levels of %starch on water these hydroxyl groups tend to associate with themselves instead of the water, leaving the water to penetrate freely into the sheet of paper resulting in very low water retention values.

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INTRODUCTION

Water retention is the ability of a coating to resist the release of water and water soluble components into the paper substrate (1). In practically all of industry, water retention of the adhesive in the coating color will become a problem at some time or another and will affect operations in the coating system. However, one must fully understand the coating system first before one can explain water retention.

A coating system is made up of a binder, also called an adhesive, a pigment and water. The continuous phase of the coating system includes water and whatever dissolves in the water; this includes some of the adhesive, mainly starch. During coating several things happen. First, the continuous phase will penetrate into the sheet of paper where the adhesive will bond it to the fibers. If too much adhesive penetrates into the sheet of paper, mottle will result. Mottle is when the adhesive migrates into the paper substrate unevenly, leaving patches of adhesive on the top of the coating that result in poor offset printing quality (2). If the binder migrates to the surface starving the paper of adhesive, picking may result. Picking is another printing term that describes the removal of coating from the sheet of paper during printing (3).

There are numerous mechanisms that contribute to vehicle penetration into the sheet of paper. Among these, the main two are; capillary migration and pressure migration (4). Capillary migration occurs immediately after the coating is placed onto the sheet of paper. Pressure migration occurs on the coater itself when hydraulic pressure is applied to transfer the coating color onto the sheet of paper.

In order to understand water retention more closely many researchers have developed water retention testers that measure the time it takes for water from the coating color to penetrate through the sheet of paper. In this experiment, a modified Warren tester was used that measures the time in seconds it takes for the water in the continuous phase of the coating to penetrate through a sheet of paper. The coating is first placed onto a metal screen contained in a small shallow pan that is connected to an ampmeter. A sheet of paper is then placed on top of the coating along with an electrode weight that is also connected to an ampmeter. When the sheet of paper contacts the coating, a timer is started that measures the time in seconds it will take for the ampmeter to travel full scale. This is a measure of water retention, which is a measure of the water penetration through the sheet of paper in seconds.

HISTORICAL BACKGROUND

Measurement of Water Retention

To study water retention successfully different methods and devices were developed. One of the easiest methods ever established was by Frost (5), which consisted of spreading a dry indicator on a test paper that is positioned on top of the coating. The time in seconds required for the water to penetrate through the test paper and react with the dry indicator is a measure of water retention.

Stephen (6) used a similar test which uses a dye in the coating color that penetrates into the base stock. The amount of penetration of the dye is measured, which is a measure of how much water penetrated into the sheet. The main disadvantage was a loss of accuracy due to the coating color ingredients.

A sonic method for measuring the extent of coating color drainage into the sheet was developed by Taylor and Dill (7). They established that the water in the coating phase will penetrate into the paper substrate and swell the paper fibers. As these paper fibers swell, the velocity at which sound passes through the paper substrate decreases. Sonic probes are placed on either side of the coated sheet which measure sorption rate. A sonic probe propagation meter equipped with a strip chart recorder is used to measure this rate of sorp-

tion, which is expressed as a percentage velocity retained after a period of coating penetration (8). Using this method, Taylor and Dill determined that viscosity is not always the most prominent factor influencing water retention, but that perhaps certain addition levels of additives have an affect on water retention.

A more recent method for measuring water retention relates moisture content in the base stock to conductivity. Mark (9) developed a static ring cell which consists of a ring cell, plexiglass stopper, plastic film and a brass plate. In this test, first the base stock is placed on the brass plate and the plastic film is placed on the paper, then the ring cell is placed on the plastic film and the coating is poured in the ring cell. The ring cell and brass plate are hooked to a power supply and an ammeter, and the plastic film is removed as the timer is started (10). The time required for a current of one mA to be reached through the base stock is a measure of water retention.

Another method similar to Mark was established by Stinchfield, Cliff, and Thomas (11), which consisted of measuring the time in seconds that it took for a current going through the sheet of paper to reach .5 mA. This device consists of a steel plate that the coating is placed on, a sheet of paper that is set on this coating and a weighted terminal is placed on top of the sheet and the procedure be-

gins. The method of testing that will be used in this project will be very similar to the one that I have described above, a modified Warren tester.

The tests just mentioned and the modified Warren tester that will be used in this project all have sources of error which must be minimized if accurate results are to be obtained. There are considered to be three main sources of error present with this tester: the temperature of the coating color, manual operation of the testing and the test paper itself. The effect of temperature is such that as the temperature of the coating color decreases, water retention increases (12). With respect to the manual operation of testing, this is an area that deals quite heavily with the operator doing the testing. The accuracy of the measurement depends on consistency in the test procedure. The test paper is just as important if not the most important parameter that must be controlled. The test paper must have homogeneous pores, uniform density and thickness, and a constant absorptive factor (13). One can see how severe and inconsistent the errors can be if one of these parameters is allowed to fluctuate. In this project, 20 lb bible paper will be used since it contains even pore size and it only requires 7-8 gm of water/m^2 to reach an endpoint, compared to coating base stock that required 30-40 gm of water/m^2 to reach an endpoint on the Warren tester (14).

STARCH AND ITS PROPOSED EFFECT ON WATER RETENTION

Starch in granular or particle form is an organic polymer of glucose consisting of amylopectin and amylose. Breaking these particles down into molecules can be done using a chemical conversion process that will penetrate into the particle, swell it enough to burst it and cause the starch molecules to disperse into a colloidal dispersion. Within this colloidal dispersion, the molecular weight of the molecule will decrease because of this cleavage of the starch chain. On all starch chains, there exists an alpha 1-4 bonding with an oxygen doing the bridging between the two chains. It is this characteristic that enables the starch chain to twist and turn giving it the flexibility needed for hydrogen bonding on other similar chains (15). When this reassociation of bonding occurs, retrodegradation becomes evident, which is the tendency of the starch molecules to reassociate with one another causing and increase in viscosity (16). Retrodegradation is affected by temperature, solids and pH primarily and is undesirable for the coating system when this interaction takes place because of the high viscosities.

Etherification does not break down the starch molecule as most common conversion systems do, but introduces so many groups into the molecule that micelles form (17). Micelles

are short chains of bundles that characteristically hold water, and thus provide an ideal means of raising water retention. Enzyme conversion of starch uses an enzyme to get into the starch granular and open it by increased swelling until it bursts. The molecular weight of the starch is directly related to the degree of enzyme conversion. As enzyme conversion increases, molecular weight and viscosity decrease (18).

When using converted starch with a clay pigment in a coating, many interactions can take place between the two. A clay particle consists of a hexoganal shape; cleaving or fracturing of this particle will give rise to 'active' areas on the surface of the particle that will absorb negative hydroxyl ions, and perhaps to form a tight water hull around the clay crystal (19). The clay particle now acts as a negatively charged particle and will adsorb positive ions to balance this charge. When starch is converted, the linear chain of the alpha 1-4 linkage is broken leaving the hydorgen and hydroxyl ions available to interact with the negatively charged clay particle. The size of the clay particle has an affect on the water holding characteristics of the clay in that the larger clay particles tend to give greater stability in the coating color and thus can achieve greater adsorption of starch molecules onto the surface of the particle (20).

Examining a closer look at the phase of liquid penetra-

tion into the sheet of paper, Beazley and Climpson (21) observed that water in the coating phase migrates at a higher rate than the adhesive, which means that the water has to move relative to the adhesive molecule. As these starch particles are interacting with clay pigments they form a network which the water phase must penetrate through. The more dispersed the starch and clay, the more contact points available on their molecules for tighter network structure. Beazley concluded saying that as conversion of starch procedes, the molecular weight will decrease by altering the length of the individual starch chains but will not alter the total weight of a given weight of starch. Therefore, the resistence of this water phase through the network of starch and clay will be independent of the molecular weight of the starch molecule and in affect, viscosity.

It is the intent of this project to establish a mechanism for water holding characteristics of binders, starch in particular. It is proposed that the amount of dispersion during and after depolmerization of starch will have a direct relationship with water retention. As the starch molecules are swollen and then mechanically or chemically torn apart they exist in a partially depolmerized state. In this state the starch chains are cleaved into branches causing the molecular weight to decrease. The decrease in molecular weight breakes the alpha 1-4 linkage and provides hydrogen bonding between other molecules such as water or clay. With moderate agita-

tion these branches are not fully separated, causing formation of conglomerates which may cause a decrease in the ability of the starch to hold water.

In this project a converted starch was prepared at low, medium and high molecular weights with similiar viscosities due to the degree of conversion or depolmerization. By introducing a dispersion apparatus using excess steam after the initial conversion it should be possible to see the affects. When chemical conversion is done normally, there exists parts of starch molecules that are conforming or sticking to one another that will leave low surface area availability of these molecules to absorb the water molecules in the coating color or onto the clay particles. Introducing dispersion by steam after conversion will not change the molecular weight of the starch but will disperse these starch conglomerates, increasing the availability of the surface area of the molecule to soak up the water. Harvslety (23) explains that more dispersed starch will spread over a greater volume and that the adhesive solution can be spread over a greater area of pigment particles.

Another interaction of slighter degree which should be mentioned, is the attraction of the water molecules to the converted starch by hydrogen bonding and hydroxyl ions. This ion attraction will play an important role upon holding the water for reduced binder migration in the coating color.

EXPERIMENTAL PROCEDURE

I. Coating Preparation Procedure

A. Clay Dispersion

1. Add 980 gm of distilled water to a stainless steel container.
2. Weigh out 1400 gm of Hydradisperse clay
3. Using the bench size Cowles dissolver, blend clay into water to produce 58% solids.

B. Starch Cooking Procedure

1. Add 760 gm of distilled water to container
2. Weigh out 210 gm of Penford Gum (250,260,280)
3. Mix starch into water and agitate for five minutes
4. Adjust pH to 6.5-7.5 if needed
5. Heat with indirect steam and slow agitation for ten minutes to a maxium temperature of 180F.

C. Enzyme Conversion

1. Add premeasured 5 ml of enzyme solution containing .2 gm of Alpha-Amylase, or Vanzyme.
2. Convert starch at 180F under low agitation for 2.5 and 5.0 minutes or considerable thinning occurs.
3. After elapsed time, add 22.5 ml of copper sulfate containing .2 gm of $CuSO_4$ (equal to weight of enzyme)
4. Turn off steam, agitate for 2 minutes to kill enzyme

D. Brookfield Viscosity

1. Cool sample to 150F, take viscosity at 100 rpm

2. Take Brookfield before and after dispersion

E. Coating Dispersion (Starch only)

1. Take a sample of converted starch and treat with excess steam for 1 minute for dispersion.

F. Coating Preparation

1. Weigh out 350 gm of converted starch at 20% solids
2. Use the dissolver to blend starch into the prepared clay slurry at low agitation for 50% solids.
3. Do index 'D'

G. Procede to test these two solutions on the modified Warren tester.

II. Coating Preparation Procedure #2

A. Clay Dispersion

1. Add 43 gm of distilled water to a stainless steel container
2. Weigh out 100 gm of Hydradisperse clay
3. Using the bench Cowles Dissolver, blend clay into water to produce 70% solids.
4. Produce four identical batches of the clay dispersion

B. Starch Cooking Procedure

1. Add 910 gm of distilled water to container
2. Weigh out 10 gm of Penford Gum 280 (1% solids)
3. Mix starch into water and agitate for 5 minutes
4. Heat with indirect steam to a maxium of 180F
5. By varying the amounts of water, produce solutions of 5, 10, and 20% solids of starch onto water.

C. Starch Testing (Starch only)

1. Take the 4 batches of starch solutions from index 'B' and test individually on the modified Warren tester.

D. Coating Preparation

1. Take 1 sample of 70% solids clay into a container
2. Adjust the amount of starch solids in index 'B' so when added to clay, starch onto water will produce 1, 5, 10, and 20% solids.
3. Mix calculated amounts of starch into clay at 70% solids.
4. Test the 1, 5, 10, and 20% starch on water individually on the modified Warren tester.

EXPERIMENTAL RESULTS

All work leading up to this point consisted of preparing starch/clay slurries at different ranges of viscosities using enzyme conversion and different levels of Penford Gum starch (250,260,280). Steam dispersion was then introduced on half of each of the samples, all viscosities recorded. The remaining part of this experiment consisted of preparing starch and starch clay slurries at different levels of %starch onto water (1,5,10 and 20%). Water retention tests were then performed on all samples using the modified Warren tester and the results are as follows.

Observing the affects that different levels of Penford Gum starch have upon viscosity and water retention before and after steam dispersion, from Table I one can see that as the levels of viscosity decrease between the different levels of starches, water retention of the slurry increases to a point.

	PENFORD GUM			ENZYME CONVERSION			
	(250)	(260)	(280)	(250)	(2.5)	(5.0)	min
VISCOSITY							
no steam	2880	1770	870	2760	480	160	
steam	885	840	375	720	210	40	
WATER RETENTION							
no steam	4.92	3.43	8.23	4.68	4.0	6.23	sec
steam	4.97	3.59	8.93	4.93	5.1	6.58	

Table I

However, at an intermediate level of viscosity, water retention values of the slurry decreases beyond that of the highest viscosity slurry. This is also prevailant in the enzyme conversion part of this procedure. As steam is introduced into the starch sample, and then mixed with a clay slurry, water retention values produced a parallel curve as to before with no steam dispersion starch samples. That is, when comparing the water retention values of the slurries in each level before and after steam dispersion, the addition of steam produced higher water retention values.

As another comparison, a sample of Penford Gum 250 was enzyme converted for 2.5, 5 minutes and 250 with no conversion. From Table I, one can see that as the level of viscosity decreases between the different levels of conversion, water retention values increased only to a point. Again, at this intermediate level of viscosity there exists an abnormal low of water retention as we saw in our earlier results. As steam is introduced into the starch system, water retention values within the converted starches increased more than when no steam dispersion was introduced.

Further work was done concerning the possible interaction that takes place between starch, clay, and water. From Figure I, one can observe the affects of poor starch dispersion vs thorough dispersion and percent starch on water alone and with clay. It is shown that with adequate starch disper-

sion water retention values are much higher as to the poorly dispersed starch solution. Also, water retention values of starch solutions on water alone were higher then the starch-clay solution with the same amount of starch onto water.

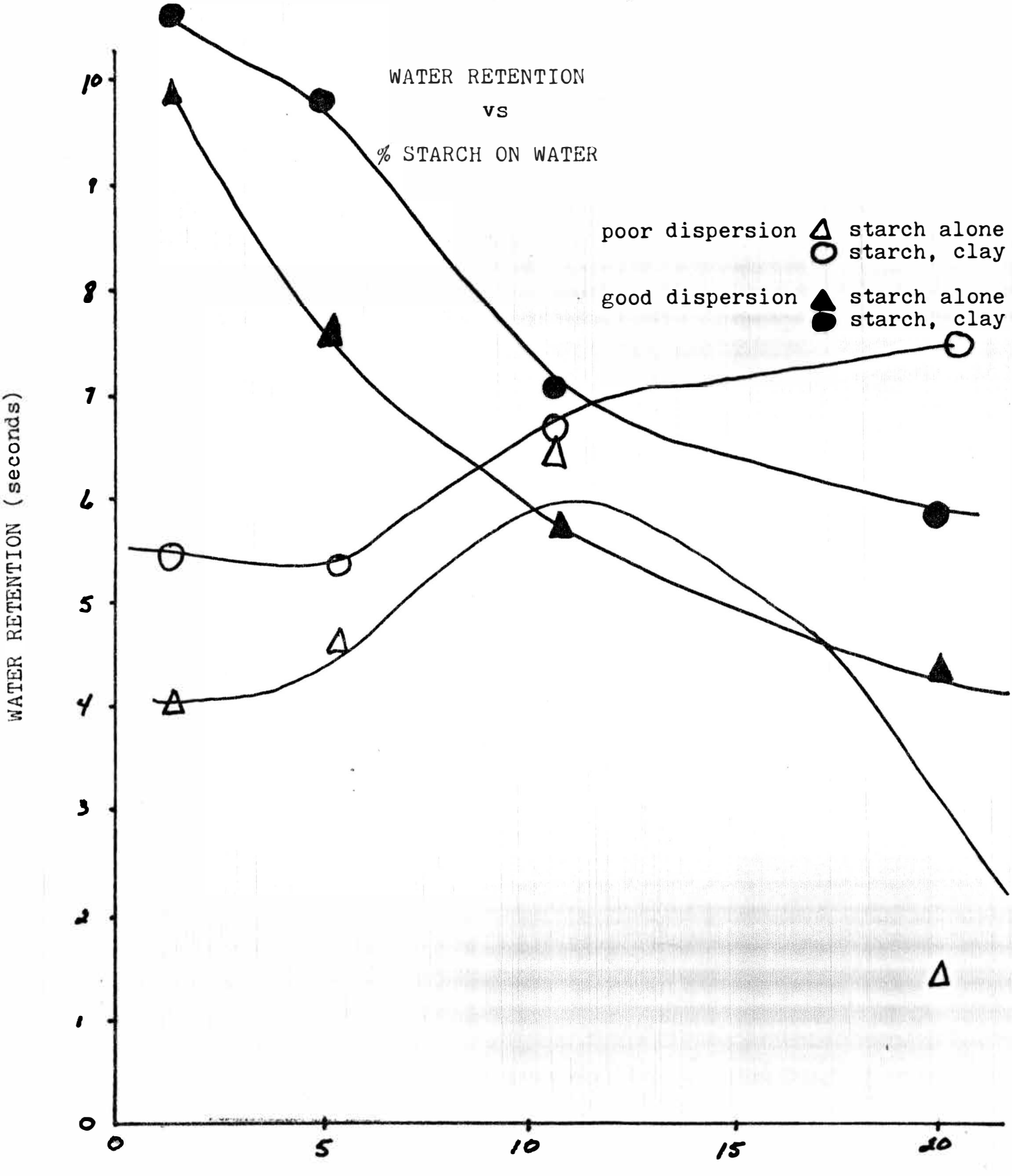
WATER RETENTION
vs
% STARCH ON WATER
poor dispersion
starch alone
starch, clay
good dispersion
starch alone
starch, clay
WATER RETENTION (seconds)
0
1
2
3
4
5
6
7
8
9
10
0
5
10
15
20
% STARCH ON WATER

Figure I

DISCUSSION OF RESULTS

As stated earlier, with the addition of excess steam for dispersion after starch conversion by enzyme or at different levels of Penford Gum (250,260,280), the viscosity of the starch/clay slurry will decrease resulting in an increase in water retention at constant molecular weight. This has been theorized in an earlier part of this discussion and comparisons to exactly what should happen and what actually did happen is the intent of this discussion.

Refering to Table II, one can see that as the viscosity of the starch solution decreases, water retention values increase except at the intermediate level of viscosity.

	PENFORD GUM			ENZYME CONVERSION			
	(250)	(260)	(280)	(250)	(2.5)	(5.0)	min
VISCOSITY no steam	2880	1700	870	2760	480	160	
WATER RETENTION no steam	4.92	3.43	8.23	4.68	4.0	6.23	sec

Table II

As the starch is more thoroughly dispersed decreasing viscosity, smaller molecules or groups of molecules are formed. These groups are then able to be carried into and

through the sheet of paper along with the water resulting in an increase in water retention. At higher viscosities (lower levels of dispersion), water is released from these groups to pass through by itself resulting in lower water retention values.

Looking at Table III, one can see little difference in water retention values before and after steam addition.

	PENFORD GUM			ENZYME CONVERSION			
	(250)	(260)	(280)	(250)	(2.5)	(5.0)	min
VISCOSITY							
no steam	2880	1770	870	2760	480	160	
steam	885	840	375	720	210	40	
WATER RETENTION							
no steam	4.92	3.43	8.23	4.68	4.0	6.23	sec
steam	4.97	3.59	8.93	4.93	5.1	6.58	
% SOLIDS							
no steam	-	17.0	18.2				
steam	-	12.8	13.5				

Table III

This small difference in data before and after steam dispersion is felt to be due to good dispersion during the initial cook. The slight increase in water retention values is felt to be caused by poor initial dispersion during the cooking of the starch. With the addition of steam after the initial cook, the starch granuals that have not been broken or cleaved will be with the addition of steam. This will provide a

greater area of binder spread and polar bonding sites onto the clay particle, creating a tight network that water must flow through for migration. If the water should flow through the starch/clay network the starch or binder will follow, but not as much if their exists a plentiful supply of bonding sites of starch onto clay by polar attraction.

With further work in this area, contained in Figure I, one can observe identical results with respect to poorly dispersed starch vs thoroughly dispersed. That is, with thoroughly dispersed starch, the starch granuals that have not been broken with poorly dispersed starch, will be broken creating greater availability of polar attraction between starch and water. However, evidence indicates that starch ions are not primarily interacting with clay but with the water. At low %starch on water, water retention values are at a maxium; a direct cause of maxium hydroxyl availability of starch onto water created by thorough dispersion. At high levels of %starch on water, water retention values decreased, result being that with increased levels of starch, starch tends to reassociate with itself more often then with the water, causing a decrease in water retention values. In other words, with thorough starch dispersion, hydroxyl ions are exposed to interact with hydrogen ions in water. The availability of these hydroxyl ions present to react with water, determine the extent of binder migration in the slurry.

CONCLUSIONS

The addition of excess steam into the starch system provides maxium dispersion of starch particles, resulting in a decrease in viscosity and an increase in water retention. Dispersion of starch has a direct relationship with water retention of the coating color, and inversly related to viscosity. That is, as steam dispersion is provided, viscosity decreases causing an increase in water retention values. As the starch is more thoroughly dispersed decreasing viscosity, smaller molecules or groups of molecules are formed. These groups are then able to be carried into and through the sheet of paper along with the water resulting in an increase in water retention. At higher viscosities (lower levels of dispersion), water is released from these groups to pass through by itself resulting in lower water retention values. It was also found that the availability of starch groups in the coating system is very important. That is, at low levels of starch on water, starch hydroxyl groups are available to entangle with the waters hydrogen groups more then at high %starch on water, resulting in high water retention values. At high levels of starch on water, the hydroxyl groups of the starch molecules self associate with themselves instead of water, creating low water retention values.

RECOMMENDATIONS

To improve this experiment, I would strongly recommend doing this procedure at higher %solids (60-65), not only is this range normal for industry, but will give improved coating stability resulting in more uniform data. Since the modified Warren tester is very sensative to temperature and pH, these two variables should be carefully measured to see the effects. Further work can be done in the area of varying the amounts of clay on water to see the interaction that may take place between the two. These recommendations that I have mentioned should change this experiment tremendously, giving way to further experimentation in this area.

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